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THE FREE ENERGY OF WATER, CARBON MONOXIDE, AND CARBON DIOXIDE

BY

E. D. EASTMAN

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THE FREE ENERGY OF WATER, CARBON MONOXIDE, AND CARBON DIOXIDE[1]

By E. D. Eastman[2]

The basic character of the free energy data relating to water and the oxides of carbon makes it desirable that the most representative values that can be obtained should be constantly available. The calculations of Lewis and Randall[3] retain much of their original value, but appear to require some modification in the light of more recent work. This paper has been written to incorporate the newer information and to present some estimate of the reliability of the resulting figures.

The data upon which the calculations are mainly based are, for these substances, the equilibrium constants of the various reactions involved. The original work relating to these equilibria has been reviewed and, where possible, weighted to correspond with its probable reliability. The differences in the results of the present from the earlier calculations are partly the consequence of this appraisal and partly of the inclusion of more extensive data, as will be indicated in detail in the succeeding sections.

In addition to the equilibrium constants, various thermal data are required which are of nearly equal importance in the formulation of the final equations. The equations adopted in this work for the specific heats of the gases concerned are those derived and discussed in another paper.[4] They represent, it is believed, a distinct improvement in accuracy in several instances, and are partly responsible for the changed results. The data relating to heat contents are, except where otherwise noted, those compiled by Bichowsky.[5]

The free energy of water is independently calculable from each of four principal equilibria. These are the dissociation of water vapor at high temperatures, the dissociations of silver and mercuric oxides, and the Deacon equilibrium. The free energies of the oxides of carbon depend in addition upon

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1 - The Bureau of Mines will welcome reprinting of this article, but requests that the following footnote acknowledgment be used: "Printed by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)"

2 - Consulting physical chemist, U. S. Bureau of Mines Pacific Experiment Station, Berkeley, Calif.

3 - Lewis, G. N., and Randall, M., Thermodynamics and the Free Energy of Chemical Substances: 1st ed., New York, 1923, 653 pp. McGraw Hill Book Co.

4 - Eastman, E. D., Specific Heats of Gases at High Temperatures: Tech. Paper 445, Bureau of Mines, 1929, 27 pp.

5 - International Critical Tables; McGraw Hill Book Co., New York. Data supplied in advance of publication through the kindness of Dr. Bichowsky.

measurements of the equilibria in the producer-gas and water-gas reactions. The experimental data concerning these reactions are discussed and the calculations outlined in the succeeding sections.

THE FREE ENERGY OF WATER

The formation of water vapor from its elements, and the equilibrium constant of the reaction, will be written

$$H_2 + 1/2\ O_2 = H_2O_{(g)}\ ;\ K_1 = (H_2O)\ /\ (H_2)\ (O_2)^{1/2}. \qquad (I)$$

Using the second degree equations for the specific heats of the gases gives

$$\Delta C_p = -2.01 - 4.33 \times 10^{-4}\ T + 1.055 \times 10^{-6}\ T^2.$$

ΔH_{291} is taken as -57,820 calories, making $\Delta H_0 = -57,227$ calories. From these values the standard free energy equation may be formulated. It is

$$\Delta F = -57,227 + 2.01\ T \ln T + 2.165 \times 10^{-4}\ T^2 - 1.76 \times 10^{-7}\ T^3 - I_1\ T \qquad (1)$$

The value of the integration constant, I_1, is to be determined with the aid of the data discussed below.

Direct Measurements of the Dissociation of Water Vapor

Nernst and von Wartenberg[6] passed steam containing varying small amounts of added oxygen and hydrogen through a porcelain bulb maintained at temperatures in the neighborhood of 1,500° K. The gases were withdrawn through a small exit tube intended for rapid chilling, and were analyzed. Lowenstein,[7] working at higher temperatures, employed a bulb of platinum as a semipermeable wall and measured equilibrium pressures of hydrogen directly. Von Wartenberg[8] employed a similar though more refined method at still higher temperatures, the bulb being of iridium. Langmuir[9] passed the reacting gases over an electrically heated filament of platinum. Equilibrium conditions were reached at the surface of the hot metal, and it was assumed that diffusion from the surface was sufficiently rapid to freeze the equilibrium. In addition to these methods, explosion methods

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6 - Nernst, W., and von Wartenberg, H., "Die Dissociation von Wasserdampf": Ztschr. phys. Chem., vol. 56, 1906, p. 534.

7 - Lowenstein, Leo, "Eine neue Methode zur Untersuchung von Gasgleichgewichten bei hohen Temperaturen": Ztschr. phys. Chem., vol 54, 1906, p. 715.

8 - Von Wartenberg, H., "Ueber die Dissociation von Wasserdampf, I": Ztschr. phys. Chem., vol. 56, 1906, pp. 513-533.

9 - Langmuir, Irving, "The dissociation of water vapor and carbon dioxide at high temperatures": Jour. Am. Chem. Soc., vol. 28, 1906, p. 1357.

have been applied by various observers.[10] It is possible that measurements of the latter type may eventually be utilized. At the present, however, there are many debatable points concerning the interpretation of such results. It has been considered best to omit them from the present calculations as not of the same order of surety as the other measurements.

The values of the integration constant of the free energy equation to which the above researches lead are shown in Table 1. Langmuir's results are sufficiently numerous to justify omission of all but the experiments he considered best. Incidentally there appears to be an error in Lewis and Randall's calculation of the first result by Lowenstein which appreciably affects their value of I, ascribed to his work.

Table 1.- Integration constants of the free energy equation for water vapor

Observer	No. of experiments	$T_{(av)}$	I_1
Nernst and von Wartenberg	2	1397	-2.46
	3	1480	-2.26
	2	1561	1/-2.55
		Weighted mean	-2.37
Lowenstein	1	1705	-2.48
	1	1783	-2.27
	1	1863	-1.72
	1	1968	1/-2.30
		Weighted mean	-2.18
von Wartenberg	5	2156	-2.48
	5	2257	-2.49
		Mean	-2.48
Langmuir	2	1325	-2.75
	2	1357	-2.65
	3	1392	-2.35
	2	1433	-2.69
	3	1474	-2.86
	2	1550	-2.78
		Mean	-2.68

1/ Values obtained from experiments less accurate than the others and given less weight in the averages.

The agreement of the various observers in Table 1 must be considered very good, since the greatest difference among them is no larger than would be produced by a difference of 10° in the temperature scales. On this account it is

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10 - For example, Bjerrum, Neils, "Die Dissociation und die spezifische Wärme von Wasserdampf bei sehr hohen Temperaturen nach Explosionsversuchen": Ztschr. phys. Chem., vol. 79, 1912, p. 513; and Siegel, Wilhelm, "Untersuchungen von Gasgleichwichten und spezifischen Wärmen nach der Explosionsmethode": Ztschr. phys. Chem., vol. 87, 1914, p. 641.

unnecessary to differentiate the methods as to reliability, and the mean of the four sets of results for I_1, -2.43, can not be unrepresentative. It is perhaps of some significance, however, that the mean of the two sets which might have been affected by incomplete "freezing," namely Langmuir's and Nernst and von Wartenberg's, actually differs in the direction to be accounted for by this error from the mean of the other experiments which could not have been affected by it. A value of -2.40 for I_1 is an acceptable weighted mean of von Wartenberg's and Lowenstein's results and has been adopted as the best estimate that can be made from these data. The standard free energy of water vapor at 298° K then becomes -54,514 calories. The uncertainty of this value is estimated as 100 to 150 calories. Employing the value of Lewis and Randall, 2,053, as the free energy of the change from liquid to vapor at 1 atmosphere at 25°, the calculated free energy of liquid water is -56,567. The corresponding calculations of Lewis and Randall gave -56,640.

Calculations Based On The Dissociation of Silver Oxide

The mean value for liquid water of -56,490 calories, calculated by Lewis and Randall from the accurately known dissociation pressures of Ag_2O in conjunction with two sets of subsidiary equilibria, requires no modification. The uncertainty in it due to errors in measurement of the equilibria is unlikely to exceed 50 calories. An error of similar magnitude may be introduced through the specific heat terms, which have not been determined by measurement and can be estimated only approximately. The total uncertainty thus should not exceed about 100 calories.

Calculations From The Dissociation Of Mercuric Oxide

Taylor and Hulett[11] have studied the equilibrium

$$Hg_{(g)} + 1/2\ O_2 = HgO\ (s)\ ;\ K_2 = 1/\ (Hg)\ (O_2)^{1/2}\ . \qquad \text{(II)}$$

Their measurements of the total equilibrium pressure extend from about 630 to 750° K, but they appear to have been reproducible only above 680. Assuming the gas phase in their experiments to consist entirely of mercury vapor and oxygen, values of K were calculated from the more reliable of the experiments, and their logarithms plotted against 1/T. From this plot log K_2 was taken as 1.075 at 680 and -0.030 at 750° K. Taking the heat of formation of mercuric oxide (from liquid mercury) at 291° K as 21,700 calories, the heat of vaporization of mercury at 415° K as 14,490[12] and using the specific heat equations adopted by Lewis and Randall the standard free energy equation for Reaction II becomes

$$\Delta F = -36,830 - 0.75\ T\ ln\ T - 0.00275T^2 + I_2T. \qquad (2)$$

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[11] - Taylor, G. B., and Hulett, G. A., "The dissociation of mercuric oxide": Jour. Phys. Chem., vol. 17, 1913, p. 565.

[12] - Folger, M. F., and Rodebush, W. H., "Heats of vaporization of mercury and cadmium": Jour. Am. Chem. Soc., vol. 45, 1923, p. 2085.

From the two values of $\log K_2$ given above, I_2 is calculated to be 56.00 and 56.33, average 56.16. For the reaction

$$Hg\ (l) = Hg\ (g), \tag{III}$$

the free energy equation is formulated as

$$\Delta F = 15{,}223 + 2.1\ T\ln T - 0.0008T^2 + I_3\ T. \tag{3}$$

From the boiling point (where $\Delta F = 0$) I_3 proves to be -37.19. Combining these data there results

$$Hg\ (l) + 1/2\ O_2 = HgO_{(s)}, \tag{IV}$$

$$\Delta F = -21{,}607 + 1.35\ T\ \ln\ T - 0.00355T^2 + 18.97T, \tag{4}$$

$$\Delta F_{298} = -13{,}977.$$

The value of the standard free energy of liquid water to which the above value leads, in conjunction with the e. m. f. of the hydrogen - mercuric oxide cell, is -56,729. Lewis and Randall found -56,540.

The principal source of the large discrepancy in these calculations is the use by Lewis and Randall of a value of the equilibrium constant of Reaction II that is not justified by Taylor and Hulett's data. The boiling point of mercury, at which their value was intended to apply, is outside the range of accurate measurement. Proper extrapolation from this range does not give the value employed by Lewis and Randall.

The accuracy of the present calculations is hard to estimate. There is evidence, however, of a hitherto unsuspected source of error in this method of obtaining the free energy of water. The above two values of the equilibrium constant of Reaction II, although good averages of Taylor and Hulett's data, gave values of the integration constant differing by 0.33 unit. The specific heat of mercuric oxide in the desired temperature range is unknown. Lewis and Randall's estimate, based on Günther's measurements at very low temperatures, may therefore be incorrect. Assuming, however, that it and the other thermal data are nearly correct, the above difference in integration constants corresponds to a deviation in the equilibrium constant of about 15 per cent over an interval of only 80°. This deviation is in the direction that would result if appreciable amounts of undissociated mercuric oxide vapor were present in the equilibrium mixtures whose total pressures were measured. The equilibrium has not been sufficiently studied to exclude this possibility. Until more is known on this point the value calculated for water from this equilibrium must be considered very much less certain than the other values, and should probably be given no weight in the final calculations.

Calculations From the Deacon Equilibrium

The Deacon reaction and its equilibrium constant will be written

$$1/2\ Cl_2\ (g) + 1/2\ H_2O(g) = HCl\ (g) + 1/4\ O_2;\ K_5 = (HCl)\ (O_2)^{1/4} / \ (Cl_2)^{1/2}\ (H_2O)^{1/2}. \qquad (V)$$

The heat of formation of HCl to be used with that previously given for water is 22,030 calories. Employing the first degree equation for the specific heat of chlorine and second degree equations for the other gases, the free energy equation becomes

$$\Delta F^o = 6847-0.05\ T\ln T-2.66 \times 10^{-4}T^2 + 8.47 \times 10^{-8}T^3 + I_5\ T. \qquad (5)$$

Four sets of equilibrium data have been discussed by Lewis and Randall from which the value of I_5 may be calculated. From them the mean value proves to be $I_5 = -7.41$, with an average deviation of about 0.15. ΔF^o_{298} becomes 4,533 and leads, employing the same subsidiary data as Lewis and Randall, to the value -56,503 calories as the standard free energy of liquid water. Lewis and Randall found -56,560.

Errors in the present calculations due to uncertainty in the equilibrium measurements are probably about 50 calories and very unlikely to exceed 100 calories. The specific heat of chlorine is not well known and may introduce 50 calories in the error. The accuracy of the above value is therefore about the same as from the direct measurements.

Average Values of Free Energy of Water

Excluding the result obtained from the mercuric oxide dissociation, which appears to require further study, the average of the results by the other methods is -56,520 for the free energy of liquid water and -54,467 for the vapor. As these are mean values of three independent results, in none of which the error is likely to be greater than 150 calories, it seems safe to set about 100 calories as the limit of uncertainty in them.

From the mean value adopted for water vapor at 298°K the final value of I in Equation 1, becomes -2.24.

WATER-GAS REACTION

The equilibrium of water-gas reaction is represented as

$$CO_2 + H_2 = CO + H_2O\ (g)\ ;\ K_6 = (CO)\ (H_2O)\ /\ (CO_2)\ (H_2). \qquad (VI)$$

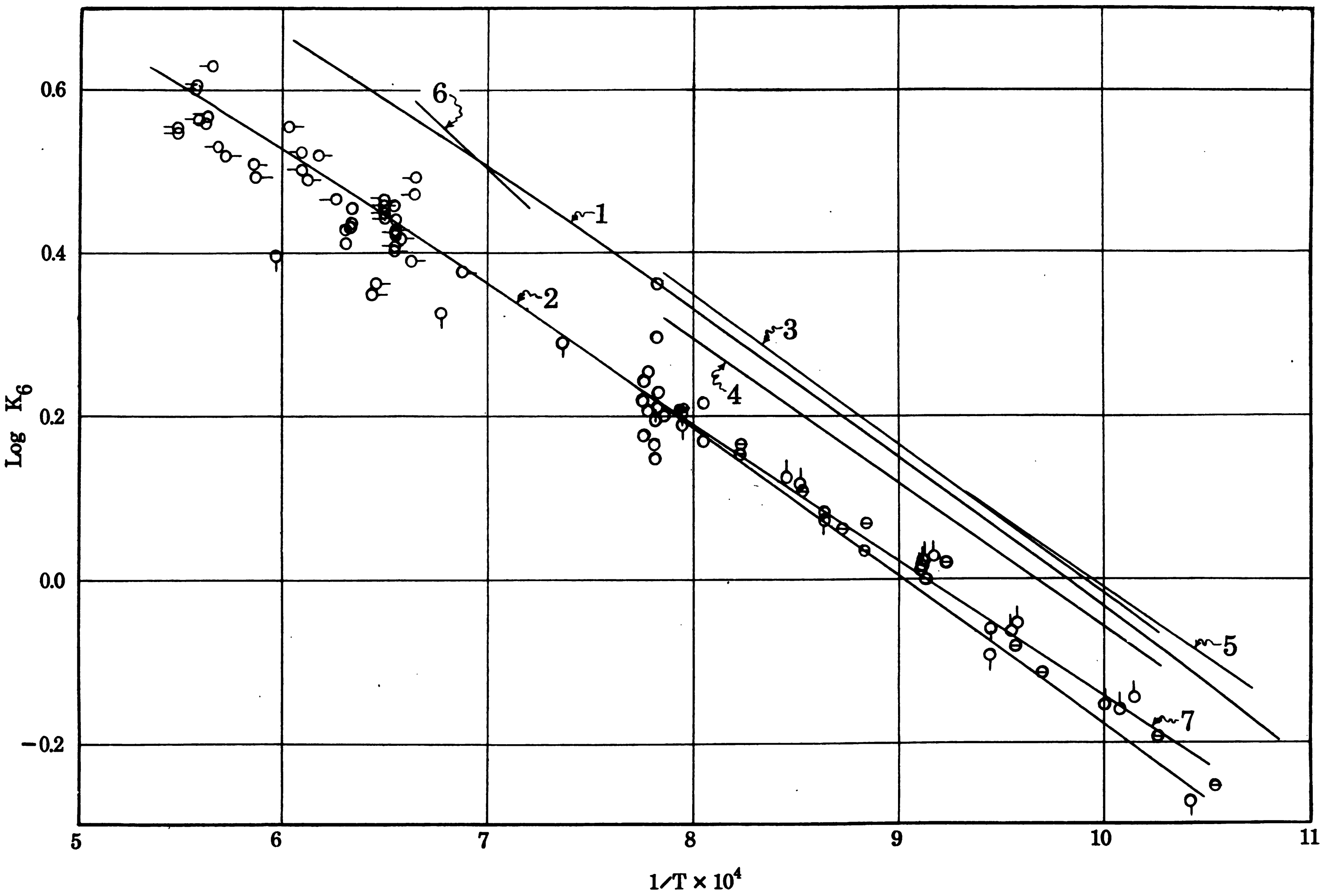

Figure 1.– Equilibrium constant of the water-gas reaction. Curve 1, Final equation (6); curve 2, Lewis and Randall; curve 3, from Fe-FeO; curve 4, FeO-Fe$_3$O$_4$; curve 5, Sn-SnO$_2$; curve 6, from H$_2$O-CO$_2$ dissociations; curve 7, average of direct results. Points by Haber and Richardt, –○ ; Allner, ○– ; Hahn, ♀ ; Engels, ♁ ; Neumann and Kohler, ⊖ ; Sullivan, ○

The heats of formation of CO and CO_2 are taken as -26,320 and -94,270,[13] which with that previously used for water give $\Delta H_{291} = 10,130$ calories. To represent the specific heat of carbon dioxide as accurately as it is known requires the cubic equation previously deduced. Employing this with the quadratic equation for the other gases, the free energy equation becomes

$$\Delta F^o = 9800 - 3.06\, T \ln T + 7.912 \times 10^{-3}\, T^2 - 2.358 \times 10^{-6} T^3 + 3.258 \times 10^{-10} T^4 + I_6 T. \qquad (6)$$

The equilibrium data which may be used for the evaluation of I_6 are now to be discussed.

Direct Determinations of Equilibrium

The numerous direct studies of the water-gas equilibrium are of two main classes. In the first of these the reacting gases are streamed over a hot catalyst, chilled as quickly as possible to freeze the equilibrium, and analyzed. Variation in the rate of flow and approach from both sides are used to test the attainment of equilibrium in the reaction chamber. In the second method, samples are withdrawn through a cooled capillary from different levels of flames produced with various gas mixtures. In both methods the success of the chilling in freezing the equilibrium is all-important. Unfortunately, it appears to be difficult to determine in all cases the degree of this success.

Observers using the first of the above methods include Hahn[14], whose catalyst was platinum, Engels[15] (iron oxide catalyst), Neuman and Köhler (cobalt oxide catalyst) and Sullivan[16] (iron catalyst). Haber andRichardt[17] and Allner[18] are the principal observers by the second method. The results of all these are shown in Figure 1. The low temperature observations of Engels and Neumann and Köhler are not, however, shown in the figure.

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13 - Roth, W. A., and Naeser, W., "Hauptversammlung der Deutschen Bunsen-Gesellschaft fuer angewandte physikalische Chemie, e. v. Ueber weissen und schwarzen Diamanten und ihr Verhältnis zum Kohlenstoff": Ztschr. Elektrochem., vol. 31, 1925, p. 461.
Dr. Bichowsky states that these values would have been accepted for the International Critical Tables had they been known at the date of closing.

14 - Hahn, Oskar, "Beiträge zur Thermodynamik des Wassergases. Das Gleichgewicht $CO_2 + H_2 = CO + H_2O$": Ztschr. phys. Chem., vol. 44, 1903, p. 513; "Nachtag zu der Untersuchungen des Gleichgewichtes $CO + H_2O = CO_2 + H_2$": Ztschr. phys. Chem., vol. 48, 1904, p. 735.

15 - Engels, --, Dessertation; Karlsruhe, 1911. Results quoted by Neumann, B., and Köhler, G., "Die Gleichgewichtsverhältnisse bei der Wassergasreaktion im Temperaturbereich von 300 bis 1,000°"; Ztschr. Elektrochem., vol. 34, 1928, p. 218.

16 - Sullivan, J. D., Unpublished results obtained at the U.S.Bureau of Mines Pacific Experiment Station, by methods similar to Hahn's, but using iron in a stream of gas of composition that did not oxidize it.

17 - Haber, F., and Richardt, F., Ueber das Wassergasgleichgewicht in der Bunsenflamme und die chemische Bestimmung von Flammentemperaturen": Ztschr. Anorg. Chem., vol. 38, 1904, p. 5.

18 - Allner, W., "Zur Kenntnis der Bunsenflamme": Jour. Gasbel., vol. 48, 1905, pp. 1035, 1057, 1081, 1107.

Indirect Determinations of the Water-Gas Constant

The water-gas constant may be indirectly determined through several independent sets of equilibrium data. Among the more important of these are the iron oxide equilibria discussed by Eastman and Evans.[19] The status of the reduction equilibria involving these oxides and hydrogen as summarized by them remains unchanged. In the reductions with carbon monoxide, both of ferro-ferric oxide to ferrous, and of ferrous oxide to iron, new work of importance has since appeared by Schenck and Dingman,[20] and Garran[21] also has published new data in these systems. To take this work into account, new average values of the constants have been determined from plots of log K vs. 1/T, including the data of the above observers, together with those of Matsubara and Eastmand and Evans. What now appear to be the "best values" of the equilibrium constants, $(CO_2) / (CO)$, in these systems are shown at 100° intervals in Table 2 below. In the fourth and seventh lines of the table are given the values of the water-gas equilibrium constant, K_6, calculated from these best values, in conjunction with the corresponding ones of the hydrogen system as originally tabulated by Eastman and Evans and repeated in the third and sixth lines. These values of K_6 are represented in Figure 1, by curves 3 and 4, respectively.

Table 2.- Constants of the reduction equilibria of iron oxides with carbon monoxide and hydrogen, and calculated water-gas equilibrium constants

Temp. °C.		700	800	900	1000
System FeO, Fe:	CO_2 / CO	0.676	0.544	0.455	0.395
	H_2O / H_2	0.584	0.706	0.822	0.937
Water gas constant,	K_6	0.864	1.30	1.81	2.37
System Fe_3O_4:	CO_2 / CO	1.84	2.56	3.43	4.36
	H_2O / H_2	1.45	2.98	5.50	9.12
Water gas constant,	K_6	0.788	1.16	1.60	2.09

Similar calculations of the water-gas constant have been made by Eastman and Robinson[22] from studies of the reactions of tin with water vapor and carbon dioxide. Their results for K_6 are represented by curve 5 of Figure 1. It will be seen that they agree well with the ferrous oxide determinations.

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[19] - Eastman, J. D., and Evans, R. M., "Equilibria involving the oxides of iron": Jour. Am. Chem. Soc., vol. 46, 1924, p. 888.

[20] - Schenck, Rudolf, and Dingman, T., "Gleichgewichtsuntersuchungen ueber die Reduktions, Oxydations, und Kohlungsvorgänge beim Eisen. III": Ztschr. anorg. Chem., vol. 166, 1927, p. 113.

[21] - Garran, R. R., "Equilibria at high temperatures in the system iron-oxygen-carbon": Trans. Faraday Soc., vol. 24, 1928, p. 201.

[22] - Eastman, E. D., and Robinson, P., "Equilibrium in the reaction of tin with water vapor and carbon dioxide": Jour. Am. Chem. Soc., vol. 50, 1928, p.1106.

A test of the water-gas constant depending upon reactions of quite a different type from the above is afforded by studies of the dissociation of carbon dioxide and water vapor. For the present purpose the data of Langmuir for these two substances are best considered independently of all others, since they were obtained by the same method and are likely to be affected[23] by about the same errors, which should therefore be partly eliminated in the calculation of the water-gas constant. Unfortunately Langmuir's experiments with carbon dioxide were limited to six. Of these he states that four "were much more carefully made" than the other two. The constants resulting from these four were plotted on log K vs. 1/T diagram, together with his more numerous data for water. From the lines chosen as best representing these data, curve 6, representing the water-gas constant in Figure 1 has been constructed. How much weight may be given to these experiments is problematical. The number of reliable experiments with carbon dioxide is small. Moreover, if the error due to incomplete freezing affects these measurements, it may not do so equally in the two cases. Nevertheless, there is general agreement of the calculated curve with the other indirectly determined ones, as shown in Figure 1.

The foregoing comprise all of the known data suitable for indirect test of the water-gas constant.[24] They will be compared with the direct result in the following paragraphs.

Comparison of Direct And Indirect Values of The Water-Gas Constant

The comparison afforded in Figure 1 of the results of these determinations reveals that each set is self-consistent but that the indirect are higher by about 40 per cent than the direct. This difference corresponds to a difference in temperature of about 100°. Errors as large as this are extremely unlikely in the indirect measurements. The large discrepancy suggests that all of the direct methods that have been used are subject to some difficultly avoidable error. It appears possible that the equilibrium in this reaction has not been satisfactorily frozen in any of the direct experiments discussed above. This condition might be brought about if the exit capillary always becomes contaminated with a layer (possibly very thin) of the catalyzer and is effective in shifting equilibrium as the gases are withdrawn. The contamination of the capillary might be effected either by the distillation of metal or oxide, or by carrying of fine particles in the gas stream. An observation of Langmuir's is perhaps significant in this connection. He found that when the platinum filament in his apparatus was heated above a particular limiting temperature, which was lower in the presence of air than in the other gas mixtures, a coating of the catalyst was deposited upon the walls of the glass tube. This coating was so thin as to be invisible, but was sufficiently effective catalytically to require cleaning or renewal of the tube before further use. An effect of this kind would be sufficient to account for the low results of the direct methods, as well as the extreme variability found with iron as a catalyst. Whether it is the true cause of the discrepancy or not, there can be little doubt that the indirect are of greater weight than the direct experiments.

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[23] - The only other sets of comparable experiments are the explosion studies. As previously pointed out, there are serious, unsettled questions concerning such experiments in measurement of equilibrium, and they have not been employed here for this reason.

[24] - There is, however, one instance in which a reversal of the test is of interest. Maier, C. G., and Ralston, O. C., "Reduction equilibria of zinc oxide and carbon monoxide": (Jour. Am. Chem. Soc., vol. 48, 1926, p. 364.) studied the reduction equilibria of ZnO and CO, and Maier, C. G., Parks, G. S., and Anderson, C. T., "The free energy of formation of zinc oxide": (Jour. Am. Chem. Soc., vol. 48, 1926, p. 2564) measured the e.m.f. of the hydrogen-zinc oxide cell. These measurements may be combined to give the free energy of the water-gas reaction at 298°K. The equilibrium experiments were attended, however, by very considerable difficulties, and the authors fixed the probable error in this one part of their work as 300 calories. The free energy of the water-gas reaction at 298°K is calculated from the zinc oxide experiments to be 7,325 calories. From Equation 6, with the value of I_6 finally chosen, it is 6,920. Lewis and Randall's equation gives 7,240. There is therefore, better support in this case for the direct than for the other indirect values, but the discrepancy is not definitely outside the possible limit of the combined error of the various measurements involved. The correctness of the zinc oxide work to the degree claimed for it is therefore supported.

For the further comparison of the direct and indirect results, and to assist in the selection of the best value of the integration constant, I_6, values of it have been calculated from the two sets of iron oxide equilibria and from the average of the direct results between 700 and 1,000°C. The direct values of the equilibrium constant required for this correspond to curve 7 of Figure 1, which was drawn as representative in this region. The values of I_6 so obtained appear in Table 3.

Table 3.- Integration constants of the free energy equation for the water-gas reaction

Temp. °C.	700	800	900	1000	Av.
I_6 from system FeO, Fe	5.51	5.52	5.54	5.54	5.53
I_6 from system Fe_3O_4, FeO	5.70	5.74	5.79	5.79	5.75
I_6 direct values	6.07	6.16	6.25	6.27	6.19

Of the indirect equilibria the most accurately known are those in the ferrous oxide-iron system. There is very close agreement in the carbon and the hydrogen equilibria among four independent observers in each case. Any doubts as to the effect of carbon upon the iron, which might render the carbon system not comparable with the hydrogen, appear to have been resolved by the work of Schenck and Dingman,[20] who showed that under the conditions of their measurements no appreciable amount of carbon was taken up by the iron phase. The constants of these equilibria must now be classed among the most accurately known of their type. It is therefore reassuring to find the extreme constancy in the values of I_6 shown in the second line of Table 3. It is difficult to see how these values can be seriously in error.

The constants in line 3 of Table 3 calculated from the systems including the two oxides are less consistent among themselves and differ somewhat from the above. These differences are not greater, however, than the possible combined errors in the separate equilibrium constants, which appear to be less reproducible than in the simpler system.

The direct values of I_6 are less constant than either of the other sets shown.

In choosing the final value of I_6 for the water-gas reaction in these calculations it is assumed that the indirect values deduced from the FeO-Fe experiments are essentially correct. The other experiments, including the direct values, are given weight only to the extent that they are assumed to indicate the direction of deviation of the former from the true values. Accordingly the largest difference that seems experimentally likely from the values in line 2 of Table 3 is allowed in the direction of the others, and I_6 is taken as 5.60.

Before leaving the discussion of the water-gas equilibrium an article on this subject by Partington and Shilling[25] should perhaps be mentioned. The equilibrium data chosen here as most nearly correct differ greatly from the data used by them, which rest upon the direct experiments. The final equations are therefore in conflict for this reason, but also because of the specific heat data employed, a point discussed in former papers. Concerning the test which they suggest of the accuracy of specific heat data by means of equilibrium measurements, it may be said that few of the latter are accurate enough for this purpose. Those that are, are unfavorable to the equations of Partington and Shilling. For an example of this, additional to the cases discussed here, reference may be made to a paper by Bäckstrom.[26]

PRODUCER GAS REACTION

The producer gas equilibrium will be written:

$$C\ (\beta\ \text{graphite}) + CO_2 = 2CO\ ;\ K_7 = (CO)^2 / (CO_2). \qquad \text{(VII)}$$

The heats of formation and specific heats of the gases required for formulation of the free energy equation are those already mentioned. The specific heat of graphite, which is also required in this case, has been determined fairly accurately by Schläpfer and DeBrunner.[27] Their results agree well with the best of the other determinations. For the present calculations two equations have been deduced. These are

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25 - Partington, J. R., and Shilling, W. G., "The water-gas equilibrium": Jour. Soc. Chem. Ind., vol. 44, 1925, p. 149.

26 - Bäckstrom, H. T. J., "The heat of dissociation of calcium carbonate and the entropy of carbon dioxide": Jour. Am. Chem. Soc., vol. 47, 1925, p. 2443. The direct comparison here is of the measurements of Dixon and Greenwood, for CO_2, which are comparable to Partington and Shilling's, with the equation of Lewis and Randall, which in this range of temperature is not very different from the one used here.

27 - Schläpfer, P., and De Brunner, P., "Zur Kenntnis der spezifischen Wärme des graphitischen Kohlenstoffes und des Kokses": Hel. Chim. Acta, vol. 7, 1924, p. 31.

$$C_p = -1.59 + 0.01556T - 1.223 \times 10^{-5} T^2 + 3.348 \times 10^{-9} T^3,$$

and

$$C_p = 1.22 + 0.00489T - 1.11 \times 10^{-6} T^2.$$

The first of these equations is closely representative of the best experimental results between 300° and 1,600° K, to which limits it must be closely restricted. The second equation is approximately right in the range where experimental measurements exist and is not far from the roughly estimated values obtained by extrapolation up to 2,500° K.

In the first calculations, when the full accuracy attainable is desired, the cubic equations for graphite and carbon dioxide will be employed, with the second degree equation for carbon monoxide. The free energy equation then becomes

$$\Delta F^0 = 39810 - 10.04 \, T \ln T + 0.01532 \, T^2 - 4.231 \times 10^{-6} T^3 + 6.048 \times 10^{-10} T^4 + I_7 T. \quad (7)$$

I_7 in this equation is determined from equilibrium data as follows.

The available studies of the producer gas equilibrium include the work of Boudouard,[28] Mayer and Jacoby,[29] Rhead and Wheeler,[30] and Jellinek and Diethelm.[31] Boudouards work, creditable as it is, should no doubt be supplanted by the later results. Among the experiments of the other investigators, a very considerable variation in conditions (nature of carbon, type of equilibrium experiments, pressure of gases) is represented. Considering this variation, the results are in very fair agreement, as will be seen from Figure 2 where they are plotted. Of all of the experiments, the second series of Rhead and Wheeler, and the recent studies at high pressures by Jellinek and Diethelm appear to be most reliable. The average integration constant from Rhead and Wheeler's measurements (second series) is about 17.18 and from Jellinek and Diethelm's is 17.05. The value adopted for the present calculations is 17.12. It appears unlikely that this value is wrong by more than 0.3. This constant is employed in the construction of Curve 1 of the figure.

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28 - Boudouard, O., "Lois numeriques des equilibres chimiques": Compt rend., vol. 130, 1900, p. 132.

29 - Mayer, M., and Jacoby, J., "Ueber einige Gasreaktionen": Jour. Gasbel., vol. 52, 1909, p. 305.

30 - Rhead, T. F. E., and Wheeler, R. V., "The effect of temperature on the equilibrium $2CO \rightleftharpoons CO_2+C$": Jour. Chem. Soc. (London), vol. 97, 1910, p. 2178; "The effect of temperature and of pressure on the equilibrium $2CO \rightleftharpoons CO_2+C$": Jour. Chem. Soc. (London), vol. 99, 1911, p. 1140.

31 - Jellinek, Karl, and Diethelm, Alois, "Ueber das Generatorgasgleichgewicht bei hohen Drucken": Ztschr. anorg. Chem., vol. 124, 1922, p. 203.

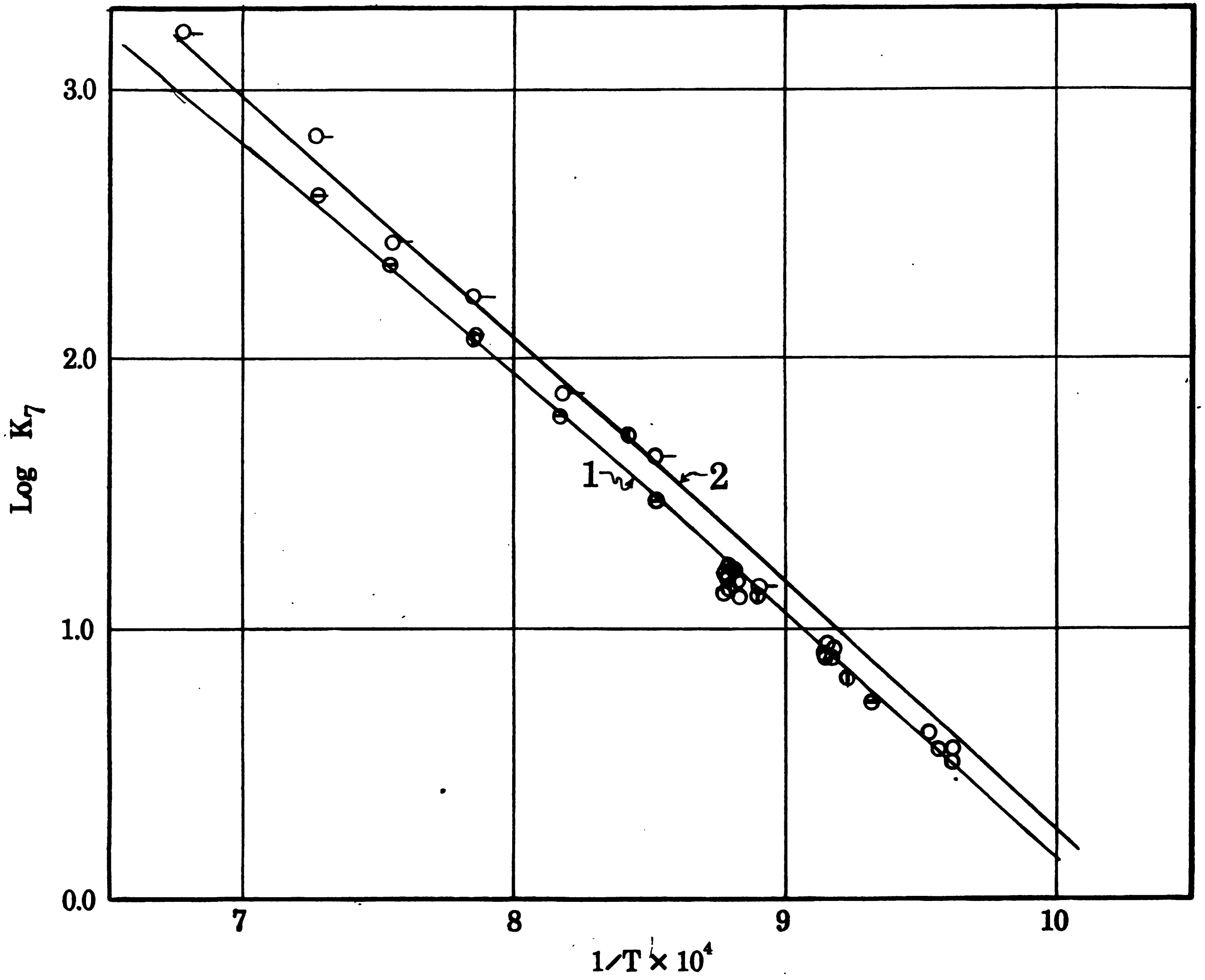

Figure 2.– Equilibrium constant of the producer-gas reaction. Curve 1, Final equation (7); curve 2, Lewis and Randall. Points by Rhead and Wheeler, first series ○– , second series ⊖; Mayer Jacoby, ○: Jellinek and Diethelm, ⦶

In addition to the studies discussed above, there are a number of measurements at lower temperatures in which a catalyst was employed. Thus Mayer and Jacoby used platinized asbestos; Falcke,[32] iron and nickel; and Schenck[33] and Juschkewitsch, cobalt. There are greater variations among these results than among the direct measurements, but their average agrees fairly well with the extrapolated values of the direct studies. In spite of this agreement the results with catalysts have not been considered in determining the value of I_7. It is difficult to see how graphite can be rendered reactive by the presence of another solid phase. Undoubtedly the function of the catalyst is the production of a different reactive phase containing carbon. It is this phase that determines the equilibrium. If the phase is pure carbon it can differ from graphite only because of its degree of subdivision which is not likely to produce large effects. But if the active phase is a carbide or solution of carbon in the metal, the graphite equilibrium is obviously not concerned. Certainly nothing is to be gained toward accelerating the equilibrium of large crystals of graphite with the gas from the presence of a solid "catalyst."

FINAL FREE ENERGY EQUATIONS

Data for the formulation of the free energy equation for water were discussed in the first section. The final equations based on these data were found to be

$$H_2 + 1/2\ O_2 = H_2O\ (g), \qquad (I)$$

$$\Delta F^0_T = -57{,}227 + 2.01\ T \ln T + 2.165 \times 10^{-4} T^2 - 1.76 \times 10^{-7} T^3 - 2.24\ T, \qquad (1)$$

$$\Delta F^0_{298} = -54{,}467.$$

$$H_2 + 1/2\ O_2 = H_2O\ (l)\ ;\ \Delta F^0_{298} = -56{,}530.$$

The equation for the vapor is valid between 300 and 2,500° K.

Employing the equation for water in conjunction with those for the water-gas and producer-gas reactions, equations for the oxides of carbon may be obtained. For carbon monoxide there is thus found

$$C\ (\beta\ \text{graphite}) + 1/2\ O_2 = CO, \qquad (VIII)$$

$$\Delta F^0_T = -27{,}217 - 4.97\ T \ln T + 7.624 \times 10^{-3} T^2 - 2.049 \times 10^{-6} T^3$$

$$+ 2.79 \times 10^{-10} T^4 + 9.28\ T, \qquad (8)$$

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32 - Falcke, V., "Hauptvessammlung der Deutschen Bunsen-Gesellschaft fuer angewandte physikalische Chemie, e.v. Die Reaktion zwischen Eisenoxydul und Kohle und zwischen Kohlenoxyd und Eisen": Ztschr. Elektrochem., vol. 22, 1916, p. 132; vol. 27, 1921, p. 268.

33 - Schenck, Rudolf, "Ueber die chemischen Gleichgewichte bei der Reduktion und zementation des Eisens": Ztschr. Elektrochem., vol. 24, 1918, p. 248.

$\Delta F^{\circ}_{298} = -32,265.$

The carbon dioxide equations become

$$C\ (\beta\ \text{graphite}) + O_2 = CO_2\ , \qquad \text{(IX)}$$

$$\Delta F^{\circ}_T = -94244 + 0.10\ T \ln T - 7.1 \times 10^{-5}\ T^2 + 1.33 \times 10^{-7}\ T^3 - 4.68 \times 10^{-11} T^4 + 1.44\ T. \qquad (9)$$

$\Delta F^{\circ}_{298} = -93,647.$

The above equations for carbon monoxide and dioxide are limited to the temperature range from 300 to 1,600°K. To obtain equations of wider range, though of somewhat lessened accuracy, the quadratic equations for specific heats, approximately correct between 300 and 2,500°K, have been used. The values of I in the resulting equations were determined from the above values of free energy at 298°. For carbon monoxide the approximate equation is

$$\Delta F^{\circ}_T = -26,764 - 2.16\ T \ln T + 2.293 \times 10^{-3}\ T^2 - 1.96 \times 10^{-7} T^3 - 6.826\ T. \qquad (8a)$$

For carbon dioxide it is

$$\Delta F^{\circ}_T = -94,182 + 0.28\ T \ln T + 9.8 \times 10^{-5}\ T^2 - 2.5 \times 10^{-8} T^3 + 0.173\ T. \qquad (9a)$$

To show to what extent the fundamental equilibria of the carbon systems are representable by the final equations chosen, the curves calculated from (1), (8), and (9) are shown in Figures 1 and 2. For comparison, similar curves calculated from Lewis and Randall's values are also shown (as curve 2 in each case). The free energy values obtained by the latter at 298° K are:

H_2O (1), − 56,560 : CO, − 32,510 ; CO_2 , − 94,260.

The uncertainty in the final results above is of course very difficult to estimate closely. However, from considerations such as the extent of agreement between different observers of equilibrium, the effect of inaccuracies in specific heat data, varying temperature scales, etc., it appears fair to estimate the uncertainty in the free energy of each of the substances as of the order of 100 calories at 300°K. This corresponds to an error of about 15 per cent at all temperatures in the equilibrium constant of a reaction involving 1 mole of any one of the substances. These uncertainties will probably not be lessened until (1) a simple low temperature determination of the free energy of water that involves no quantities of unknown magnitude is available, and (2) more precision of temperature measurement and control is introduced into high-temperature determinations of equilibrium such as the producer-gas studies. Further, as long as the cause of the discrepancy between the direct and indirect determinations of the water-gas constant is in doubt, the situation must remain not completely satisfactory, since there is then always a remote chance that much larger errors than those estimated are present.

SUMMARY

The fundamental equilibrium data upon which the free energies of water, carbon monoxide, and carbon dioxide depend have been critically reviewed. From the data selected as most reliable, in conjunction with improved specific heat equations and the best available thermochemical data, the free energies of these substances have been calculated. The final results, as well as those in most of the subsidiary calculations, differ appreciably from those now generally accepted. An attempt has been made to estimate the order of the errors in the present calculations.

In two of the equilibria concerned, elements of uncertainty are found that appear worthy of further study. Thus it is suggested that the exact nature of the system in the mercuric oxide dissociation may not be as simple as it has been assumed to be; in the water-gas equilibrium the direct and indirect studies lead to very different results, for which no certain explanation is apparent, although a possible one is suggested. The indirect studies appear more reliable than the direct and have been used here.

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